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Adsorption-Thermal Desorption as a Method for the Determination of Low Levels of Aqueous Organics

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16. ABSTRACT

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ADSORPTION–THERMAL DESORPTION AS A METHOD FOR THE DETERMINATION OF LOW LEVELS OF AQUEOUS ORGANICS

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SUMMARY

Adsorption followed by thermal desorption (ATD) with Tenax GC is an effective analytical tool for the preconcentration–analysis of water samples containing μg/kg quantities of the three United States Environmental Protection Agency (U.S. EPA) "Priority Pollutants" *p*-dichlorobenzene, hexachloro-1,3-butadiene, and 2-chloronaphthalene. A centrifugation method allows the removal of all but 80 μl of water from a glass cartridge packed with 0.75 g Tenax GC. A 10-min follow-up vacuum-desiccation step will reduce the residual water to ≈ 5 μl. A new procedure is presented for conducting recovery tests with sparingly soluble compounds and for the desorption of loaded cartridges. The recovery efficiencies for the three compounds showed little dependence upon the sample flow-rate in the range 0.25–2.0 ml/sec. One cartridge adsorbed ≈ 80% of these compounds at all flow-rates, and a second cartridge in series recovered the remaining ≈ 20%.

INTRODUCTION

Several analytical procedures have been developed for the analysis of trace organics in water, including purge and trap[1], "Grob stripping"[2], solvent extraction[3], and adsorption onto a solid support, such as the Amberlite XAD resins, followed by solvent extraction[4]. A fifth technique, adsorption from aqueous solution onto a solid support followed by thermal desorption (ATD), although very promising for certain types of analyses[5–10], has not been studied extensively. Three conclusions may be drawn:

(1) The inert gas purging methods are effective for many of the volatile organic compounds.

(2) Solvent-extraction-based methods do not allow equal ease of determination for compounds of relatively low volatility.

(3) ATD presents an attractive method for the analysis of compounds of low to intermediate volatility. It does not require solvents, and provides for maximum sensitivity since all of the adsorbed organics may be desorbed onto the analytical gas chromatographic (GC) column.

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Rationale for the development of ATD with Tenax GC

The fact that ATD has not developed into an accepted analytical technique for aqueous samples is due to the difficulties experienced during early research with:

(1) The extremely high blank levels associated with the thermal desorption of resin adsorbents such as the styrene-divinylbenzene polymer Amberlite XAD-2[11]. (Modified XAD-4 polymers can be synthesized which have lower blank levels[6].)

(2) The tendency for the activated charcoal adsorbents to retain many organics and catalyze their degradation[12].

(3) The relatively low specific surface area (10–30 m^2/gram[13,14]) of the adsorbent Tenax GC.

(4) The retention of water in the inter-particle void volume of the cartridge as well as within the particles of adsorbent, and the problems which this water poses for columns and detectors (*e.g.*, the flame ionization detector (FID) and the mass spectrometer (MS)).

The use of Tenax GC as the adsorbent in aqueous ATD alleviates the first and second problems. This material, poly(2,6-diphenyl-paraphenylene oxide)[15] is stable up to temperatures of 350°C, exhibits very low blank levels on thermal desorption[11,15], and has been used extensively in the ATD analysis of the atmospheric environment[16–18]. Problems posed by water on the adsorbent may be circumvented by drying the cartridge prior to desorption. Versino *et al.*[8] have shown that storage of Tenax GC cartridge tubes over the desiccant P_2O_5 at 10 Torr for 24 h is an effective drying procedure which gives 99% recoveries at the μg level, even for volatile compounds such as benzene. If the cartridge is thermally desorbed directly onto a capillary column which is at sub-0°C temperatures, this type of thorough desiccation will be required to avoid plugging the column with ice. If focussing at such low temperatures is not required, complete desiccation may not be necessary as fused silica columns are now available which are reportedly stable to repeated loadings of low μl amounts of water[19].

At 19–30 m^2/g (refs. 13 and 14), Tenax GC does not have as high a specific surface area as desired in an adsorbent, and it probably has a lower capacity for most organics than do the styrene–divinylbenzene polymers XAD-2 (290–330 m^2/g)[20] and XAD-4 (750 m^2/g)[21]. Nevertheless, in studies using solvent extraction as the recovery step, Leoni and co-workers[22,23] have found Tenax GC to be very retentive of pesticides such as γ-BHC and DDT as well as the polychlorinated biphenyls (PCBs) and several polynuclear aromatic hydrocarbons (PAHs). Therefore, although Tenax GC is both thermally stable at elevated temperatures as well as adsorptive of non-polar, aqueous organics, the potential of ATD with this material has not been developed beyond the preliminary investigations carried out by earlier workers[8,10].

The three compounds *p*-dichlorobenzene, hexachloro-1,3-butadiene, and 2-chloronaphthalene have been chosen as model compounds. Chlorinated organics are often found as contaminants in drinking waters[24]; these compounds are of particular interest since they are among the "base–neutrals" in the U.S. EPA Priority Pollutant List and in many cases must be determined by solvent extraction procedures. This paper will demonstrate the applicability of ATD with Tenax GC to the preconcentration–analysis of compounds such as these.

EXPERIMENTAL APPROACH

Recovery tests

Many organic pollutants of interest have solubilities in the low ppm range, and those of *p*-dichlorobenzene, hexachloro-1,3-butadiene, and 2-chloronaphthalene are 79[25], 2[26], and 7 ppm[27], respectively. (The solubilities of the other organic Priority Pollutants have recently been compiled by Callahan *et al.*[27]). In the determination of the efficiency of solvent extraction or inert gas purging procedures, one may simply spike the solution to be assayed. Material which is lost to the vessel walls may be recovered during the execution of the method. In the examination of cartridge adsorption efficiencies, however, such wall losses will not be recovered. We have adopted a method which circumvents this problem. It involves injecting a small volume ($\approx \mu$l) of water-miscible solvent containing μg quantities of the analytes into a stream of water which then passes on to the cartridge. While this approach does not simulate what occurs when the same overall volume of water containing the same amount of dissolved analyte(s) is passed through a cartridge, it will provide a *lower* bound on the retention efficiencies since: (1) the analytes flow on in one slug and the adsorbent is then washed by analyte-free water; and (2) the small amount of solvent injected may tend to help retain some portion of the analyte(s) in solution as the slug passes through the resin bed. We included a cartridge of tightly packed glass wool between the first Tenax GC cartridge and the injection port to retain any particles of analyte which might precipitate during this injection process. Their rapid re-solubilization would then take place in a manner similar to what occurs in the "generator columns" recently conceived for the preparation of low-level aqueous standards of sparingly soluble PAHs[28]. The occurrence of irreversible adsorption on the glass wool may be ruled out if all of the analyte materials are recovered from the cartridges.

Cartridge desiccation

While the 24-h vacuum desiccation of Versino *et al.*[8] appeared to be too time-consuming, the simple passage of a high velocity stream of nitrogen through the cartridges to dislodge the water as done by other workers seemed incapable of providing adequate desiccation. We have investigated a two-step desiccation procedure. The first step utilizes centrifugation to remove the bulk of the water, and the second step involves evacuating the cartridge for a 10–20 min period of time.

Cartridge desorption

Many methods and devices have been proposed in the literature for the desorption of sorbent cartridges into GC systems. A considerable amount of this work has been carried out by researchers involved in the analysis of trace organics in air. The simplest approach has been to insert a loaded sorbent cartridge before the GC column using compression fittings such as those marketed under the tradename Swagelok (Crawford Fitting, Solon, OH, U.S.A.)[5,10,11,31,33,36]. After a suitable purge time for the removal of any oxygen which may have entered the system, the cartridge is flash desorbed by thermal means. Resistively heated wire and tape[31] and ovens which slide over the cartridge[10,11,36] provide the heat. Although this interfacing method is simple, it is cumbersome in practice due to the nut loosening, nut tightening, and leak testing required.

A second class of desorption device utilizes a capped injector-type chamber[16,29,30] maintained at the desorption temperature. The cartridge is inserted, and a flow of carrier-gas transfers the analytes onto either an intermediate trap (a second sorbent bed or a cooled capillary line) for focussing[16,29,30] or directly onto the head of the analytical column. The disadvantages are: (1) no provision is made for purging oxygen from the cartridge prior to its desorption; (2) the cartridge does not make a positive seal in the chamber to the carrier gas supply, therefore close tolerances must be maintained in order that the majority of the desorption flow passes through the cartridge in a reproducible manner from cartridge to cartridge, and not merely via the annular space between the cartridge and the chamber; and (3) contaminants on the outside of the cartridge may enter the analytical column via whatever flow is passing through this annular space.

The desorption apparatus which we have constructed does not suffer from these deficiencies. The exchange of one cartridge for another does not require the removal of ferrule type fittings, and yet a positive seal is made between the cartridge and the analytical column. Furthermore, provision is made for the removal of oxygen from the cartridge prior to desorption.

EXPERIMENTAL

Cartridge preparation

The cartridges were of Pyrex glass (Corning Glass, Corning, NY, U.S.A.). The bed length, I.D., and O.D., were 7.0, 0.9, and 1.25 cm, respectively. A 1.5-cm piece of 2.0 mm I.D., 6.4 mm (0.25 in.) O.D. glass tubing was fused to each end of this main body. The overall length of a cartridge was 10.0 cm. The cartridges were packed with approximately 0.75 g of 35–60 mesh Tenax GC obtained from Alltech Assoc. (Los Altos, CA, U.S.A.). The Tenax GC was held in place with silanized glass wool (Supelco, Bellefonte, PA, U.S.A.). After passing a 20-ml/min flow of nitrogen (precleaned with charcoal and molecular sieve 5A (Chemical Research Services, Addison, IL, U.S.A.)) for 60 min to remove oxygen, the cartridges were conditioned for 60 min at 280°C. They were then cooled quickly, removed from the nitrogen flow, and sealed with 1/4-in. Swagelok end caps with TFE Teflon® ferrules.

Recovery tests

The apparatus used in recovery tests is presented in Fig. 1. The water used to fill the reservoir was obtained from a Millipore (Bedford, MA, U.S.A.) Super-Q water purification system. This system contains an activated carbon bed in addition to ion-exchange beds. The gases occupying the cartridge void volumes were first removed by setting the peristaltic pump at a fast flow-rate ($\approx$ 4–5 ml/sec) for approximately one min. The flow-rate for a given experiment was then set, and 4 μl of the 0.5-μg/μl standard (in acetone) was injected through the septum. After the passage of the first liter of water, the second Tenax GC cartridge was replaced with an identical cartridge and a second liter of water was passed through the system. Two more liters of water were then passed only through the first cartridge. All three of the cartridges were then desiccated and analyzed.

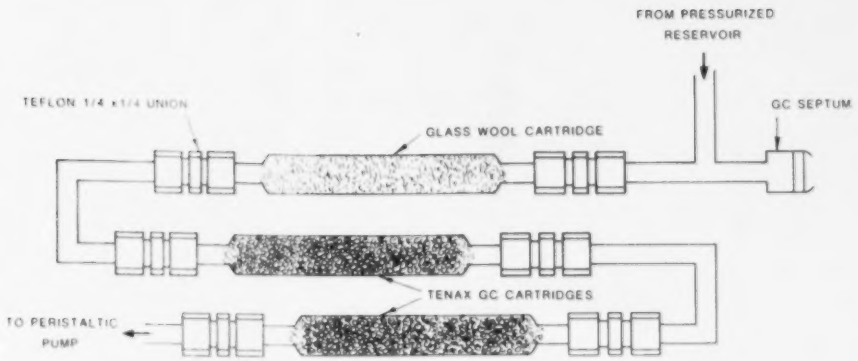

Fig. 1. Apparatus used for recovery tests.

Cartridge desiccation

A wet cartridge was first spun at 3500 rpm for 10 min in a screw cap Pyrex culture centrifuge tube previously cleaned by heating to 500°C in a muffle furnace. The screw cap liner and a set of two supporters were TFE Teflon (see Fig. 2). In some cases, additional water was removed with the apparatus presented in Fig. 3. The liquid nitrogen (LN_2) trap was included to protect the pump as well as to protect the cartridge from contaminants in the vacuum line. With both values closed, the cap was removed and the cartridge inserted. The valve on the vacuum line was then opened. After desiccation, this snap valve was again closed and the vacuum within the apparatus relieved via the second snap valve.

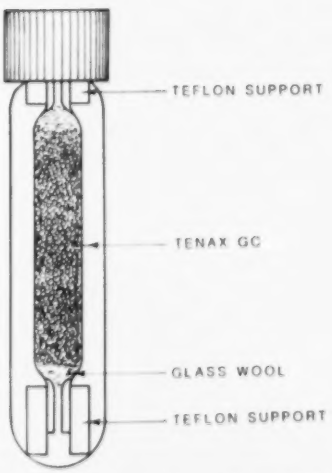

Fig. 2. Assembled culture tube for 3500 rpm centrifugation desiccation of adsorbent cartridges. Cap liner and cartridge supporters are of TFE Teflon ®.

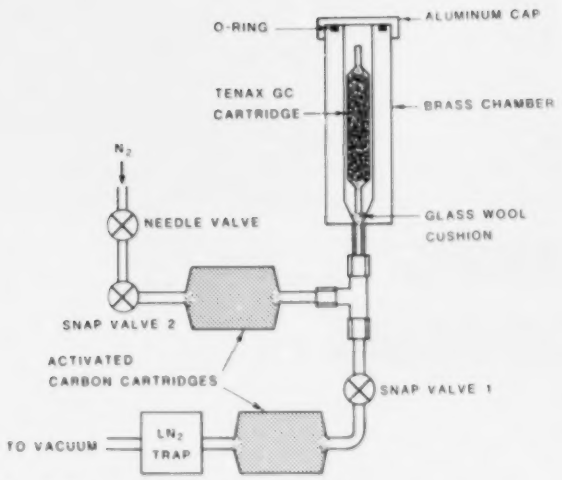

Fig. 3. Vacuum desiccation apparatus.

Cartridge desorption

The desorption apparatus which we have developed is presented in Fig. 4. This apparatus possesses several positive design features. They are:

(1) One gasket provides all necessary sealing. This gasket is made by punching out a 0.50-in. diameter hole from the center of a 0.75-in. diameter Teflon-backed Type F-174 GC septum obtained from Canton Bio-Medical Products (Boulder, CO, U.S.A.).

(2) Near all-brass construction provides for rapid heat conduction during thermal desorption.

(3) Cartridge and GC column may be butted up against one another.

(4) Upper and lower "septum" sweep lines prevent bleed contamination from septum sealing gasket. Upper sweep line also removes contaminants desorbed from exterior walls of cartridge.

(5) The desorbed analytes need not pass through any heated valving.

The following standard operation procedure (SOP) describes the use of this apparatus:

Step		*Comments*	
(1)	Turn off GC fan.	(1)	Helps to maintain high temperature in section of desorption apparatus which extends into GC oven.
(2)	Unscrew top knob, lift off brass desorption chamber, and remove previously desorbed cartridge.	(2)	–
(3)	Close snap-valve on line D.	(3)	Prevents carrier gas flow out of top of cartridge. This would occur if line D were left open and until such time that the brass desorption chamber had become pressurized.

(4)	Insert new cartridge and reverse step 2.	(4)	–
(5)	Purge cartridge 10 min with nitrogen. Flows: line A, 30 ml/min line B, 3 ml/min line C, 3 ml/min line D, 0 ml/min for first 3 min, then 5 ml/min line E, 0 ml/min	(5)	Removes O_2 from cartridge and column.
(6)	Open snap-valve on line D 3 min into O_2 purge time. (See step 5.)	(6)	Returns lower septum sweep flow and ensures that all desorption flow is on column.
(7)	Lower oven for 15 min. Flows same as in step 5.	(7)	Desorption.
(8)	Raise oven. Flows: line A, 0 ml/min line B, 3 ml/min line C, 3 ml/min line D, 5 ml/min line E, 30 ml/min	(8)	Carrier flow returned directly to column. Note continued upper septum sweep flow due to back flushing of cartridge.
(9)	Start temperature program GC run.	(9)	–

Gas chromatography

The oven top of a model 5700 Hewlett-Packard (Avondale, PA, U.S.A.) gas chromatograph was modified to accept the desorption apparatus. A 1.5 m × 2 mm I.D. glass GC column packed with 35–60 mesh Tenax GC was connected directly to the desorption apparatus with a graphite/vespel ferrule (Alltech Assoc.). During a GC analysis, the carrier gas, hydrogen, and air flow rates were 29 ml/min, 30 ml/min, and 240 ml/min, respectively. The detector temperature was 300 C. The column was at ambient temperature during the desorption of the cartridge. Following a desorption, the GC run was carried out using a temperature program run from 60 to 250 C at 16 /min. Chromatograms were recorded and peaks integrated with a Model 4100 Spectra-Physics (Santa Clara, CA, U.S.A.) computing integrator.

RESULTS AND DISCUSSION

Cartridge desiccation–centrifugation step

The cartridge desiccation procedure used for the bulk of the analyses involved only the centrifugation step. The amount of water remaining after this step was generally in the vicinity of 80 μl. This caused the formation of visible amounts of condensation within the packed column. Upon the initiation of the temperature program, this water did not extinguish the FID, nor did it interfere with these analyses since the first of the compounds to elute, *p*-dichlorobenzene, appeared in the temperature program at approximately 150 C. This is after all of the water had vaporized and left the column, and therefore we experienced no difficulty with this water interfering with the detector response for these compounds. The evaporative loss of the analyte compounds during the centrifugation step was also not a problem.

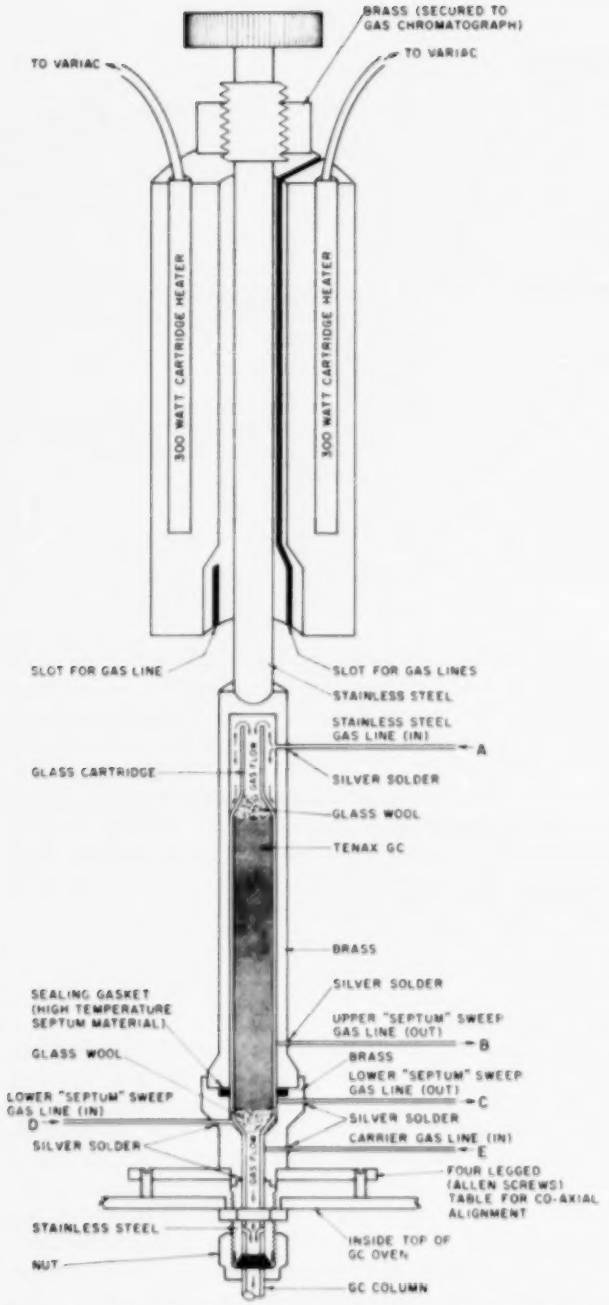

Fig. 4. Cartridge desorption apparatus. Desorption temperature is 280 C.

TABLE I

WEIGHT LOSS FROM A PRE-WETTED, CENTRIFUGE-DESICCATED TENAX GC CARTRIDGE SUBJECTED TO VACUUM DESICCATION

Time (min)	*Cartridge weight (g)*	*Cartridge weight change (g)*	*Water remaining (μl)*
0	10.6530	–	
2			79.7
4	10.6355	0.0175	
6	10.6129	0.0226	62.2
8	10.5981	0.0148	39.6
10	10.5871	0.0110	24.8
12	10.5784	0.0087	13.8
14	10.5746	0.0038	5.1
16	10.5743	0.0003	1.3
	10.5742	0.0001	1.0
After thermal desorption at 280 C	10.5733	0.0009	0.9
			0.0

Peak areas for runs in which a standard was injected directly onto fully wetted cartridges which were then centrifuge-desiccated and analyzed were found to be equal, within experimental error, to the peak areas obtained when the same amount of standard was placed onto pre-wetted, pre-centrifuge-desiccated cartridges.

Cartridge desiccation–evacuation step

Not all compounds of interest are retained on a Tenax GC column at temperatures exceeding the boiling point of water. Moreover, not all packed-column stationary phases are stable to μl amounts of water, and certainly 80 μl would preclude the use of capillary columns. An experiment was conducted to determine the rate at which a vacuum will remove the residual water. A centrifuge-desiccated cartridge containing 79.7 μl of water was vacuum-desiccated for a succession of 2-min periods (Table I). Approximately 94% of the ≈ 80 μl is removed in 10 min. We therefore chose 10 min as the standard desiccation period in a series of experiments designed to determine whether vacuum desiccation would cause a range of compounds to be lost from the Tenax GC cartridges.

Table II presents the percent recoveries observed for 2 μg of each of the compounds loaded onto pre-wetted, centrifuge-desiccated, then vacuum-desiccated cartridges. The desorptions were performed as discussed in the experimental section. These data indicate that vacuum desiccation does not cause significant loss for a variety of compound classes. They are also in agreement with the results of Versino *et al.*[8] (24 h evacuation) as well as research in the analysis of organics in air where Tenax GC has shown good retention properties during cartridge storage. The slight "losses" observed for tetracosane and methyl eicosanoate reflect a need for a longer cartridge desorption time with high molecular weight compounds.

The combination of centrifugation and vacuum desiccation is an effective procedure for the desiccation of fully-wetted cartridges. For packed-column work, a 10-

TABLE II

RECOVERY EFFICIENCIES FOR VARIOUS COMPOUNDS LOADED ONTO PRE-WETTED, CENTRIFUGE-DESICCATED TENAX GC CARTRIDGES

Compound			*Recovery (%)*
Aromatics	Benzene	C_6H_6	98 ± 1
	Toluene	C_7H_8	98 ± 1
	Xylene	C_8H_{10}	97 ± 1
Chlorinated hydrocarbons	*p*-Dichlorobenzene	$C_6H_4Cl_2$	95 ± ?
	Hexachlorobutadiene	C_4Cl_6	96 ± 1
	2-Chloronaphthalene	$C_{10}H_7Cl$	96 ± 1
Alkanes	Decane	$C_{10}H_{22}$	103 ± 0.5
	Tetradecane	$C_{14}H_{30}$	100 ± 0.5
	Hexadecane	$C_{16}H_{34}$	100 ± 0.5
	Docosane	$C_{22}H_{46}$	100 ± 1
	Tetracosane	$C_{24}H_{50}$	92 ± 5
Methyl esters of fatty acids	Methyl octanoate (methyl caprylate)	$C_9H_{18}O_2$	100 ± 1
	Methyl hendecanoate (methyl undecanoate)	$C_{12}H_{24}O_2$	100 ± 1
	Methyl tetradecanoate (methyl myristate)	$C_{15}H_{30}O_2$	100 ± 1
	Methyl octadecanoate (methyl stearate)	$C_{19}H_{38}O_2$	100 ± 1
	Methyl eicosanoate (methyl arachidate)	$C_{21}H_{42}O_2$	96 ± 1

min evacuation period is adequate if 1 to 5 μl of water may be tolerated. For capillary column work, a longer evacuation period may be required, particularly if sub-0 C focussing is needed.

Desorption efficiencies

Standards in acetone were used to place amounts ranging between 0.2–2.0 μg per component into the upper ends (as viewed in the desorption apparatus) of pre-wetted, centrifuge-desiccated cartridges. These cartridges were then desorbed and analyzed (Fig. 5). The fact that each of the plots is linear with a slope close to one indicates that: (1) the desorption efficiencies are linear across the mass range studied; and (2) a linear–linear plotting of the data would indicate zero response for zero mass.

When the desorption apparatus was first put into regular use, we felt that when the oven was first lowered, the ballistic temperature rise might caused the water remaining on the cartridge to volatilize so rapidly that the gas flow would back up in the cartridge and that a portion of the analyte(s) might thereby be lost to the surrounding brass enclosure. Since the cartridges analyzed in this series had been spiked on their upper ends, and since the analyses of spiked dry cartridges gave the same area/μg response factors, this was not problematic with the compounds studied. The fact that we saw little difference in the peak areas for cartridges which were spiked on

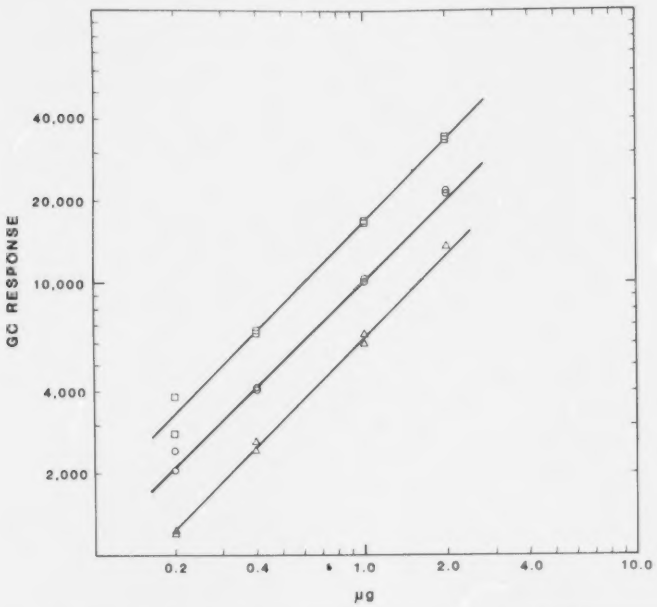

Fig. 5. Calibration plots for the desorption of varying amounts of *p*-dichlorobenzene (○), hexachloro-1,3-butadiene (△), and 2-chloronaphthalene (□). Plots are linear with slopes close to one.

the top *vs.* those spiked on the bottom indicates that desorption occurs equally well regardless of the physical distribution of the analyte(s) on the cartridges.

Recovery tests from water

A series of experiments was carried out at flow-rates of 0.25, 0.50, 1.0, and 2.0 ml/sec. A 4.0-μl volume of an acetone solution containing 0.5 μg/μl of each of the model compounds was injected at time zero. Fig. 6a–c are GC chromatograms from an experiment carried out at a flow-rate of 1.0 ml/sec. Fig. 6a is for the primary cartridge after 4 l had passed through. Fig. 6b is for the secondary cartridge, which was exposed to only the first of these 4 l, and Fig. 6c is for the secondary cartridge which was exposed to only the second of these 4 l. Fig. 7 is for the direct desorption of 4.0 μl of the acetone standard placed on the bottom of a pre-wetted, centrifuge-desiccated cartridge. The broad solvent peak is a result of the inability of the Tenax GC to retain the acetone at the head of the column during the desorption step. The retention times of the model compounds *p*-dichlorobenzene, hexachloro-1,3-butadiene, and 2-chloronaphthalene were approximately 9.5, 10.8, and 12.8 min, respectively. The relative magnitudes of the peak areas in Fig. 7 demonstrate the effects of chlorination on FID response factors. A variety of other peaks due to contaminants in the water and in the acetone are also present.

An examination of Figures 6a-c indicates that portions of these analytes escape the first cartridge and are retained on the second. However, this loss does not continue during the passage of the second liter (Fig. 6c) and seems related to the initial

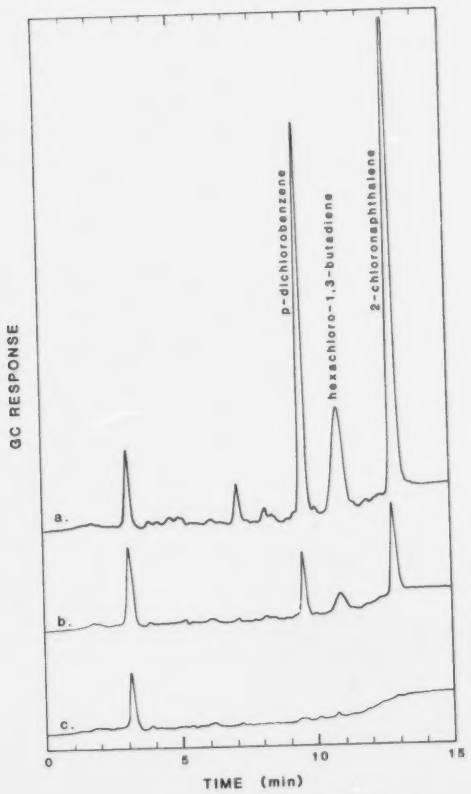

Fig. 6. Recovery from water of *p*-dichlorobenzene, hexachloro-1,3-butadiene, and 2-chloronaphthalene at 1.0 ml/sec. Attenuation = 128, or $128 \times 5 \times 10^{-12}$ A full scale for chromatogram a. a: Primary cartridge after 4 l. b: Secondary cartridge exposed to first of 4 l passing through primary cartridge. c: Secondary cartridge exposed to second of 4 l passing through primary cartridge.

injection. Remarkably, as Table III indicates, the percentage recovery (based on the desorption of a wet cartridge spiked on the bottom) did not appear to be a strong function of flow-rate. The recoveries based on the primary cartridge alone hover very near to 80%, and the recoveries including that retained on the first secondary cartridge are generally close to 100%.

CONCLUSIONS

The results obtained with a new type of desorption apparatus indicate that Tenax GC can retain non-polar organics of intermediate molecular weight very well even when substantial amounts (*e.g.*, 4 l) of water pass through the cartridges. Since flow-rates of ≈ 2 ml/sec are possible, a liter of water may be processed in only 8 min. This method is therefore simple, sensitive, and expedient, and will be applicable in the analysis of a wide variety of aqueous organic compounds.

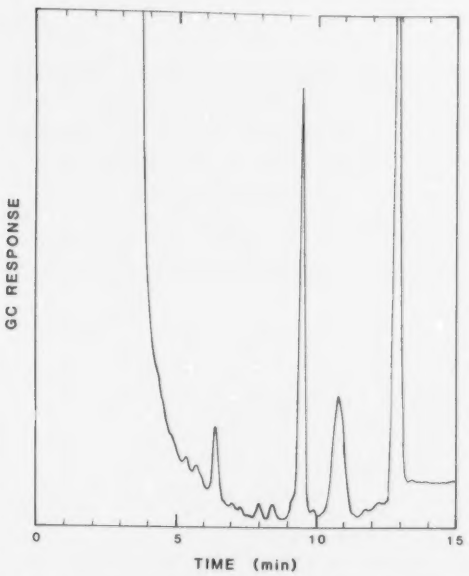

Fig. 7. Desorption of 4.0 μl acetone solution (containing 0.5 μg/μl per component) placed directly on bottom of pre-wetted and centrifuge-desiccated cartridge. Note solvent peak from acetone as for typical GC injection. This solvent peak is absent in Fig. 6. Attenuation = 128, or 128 × 5 × 10^{-12} A full scale for this chromatogram.

TABLE III

RECOVERY EFFICIENCIES AS A FUNCTION OF FLOW-RATE FOR *p*-DICHLOROBENZENE, HEXACHLORO-1,3-BUTADIENE, AND 2-CHLORONAPHTHALENE

Flow-rate (ml/sec)	*Compound*	*Recoveries (%)*	
		$\frac{\text{Primary cartridge}}{\text{Standard run}} \times 100$	$\frac{\text{Primary + first secondary cartridge}}{\text{Standard run}} \times 100$
0.25	*p*-Dichlorobenzene	86	101
	Hexachloro-1,3-butadiene	87	105
	2-Chloronaphthalene	81	98
0.5	*p*-Dichlorobenzene	76	87
	Hexachloro-1,3-butadiene	77	92
	2-Chloronaphthalene	83	99
1.0	*p*-Dichlorobenzene	80	92
	Hexachloro-1,3-butadiene	90	105
	2-Chloronaphthalene	78	91
2.0	*p*-Dichlorobenzene	81	100
	Hexachloro-1,3-butadiene	82	102
	2-Chloronaphthalene	74	94

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